Chemistry of Nanoscale Semiconductor Clusters

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Abstract

The ground state structures of small silicon clusters are determined through exhaustive tight-binding molecular dynamics simulation studies. These simulations revealed that Si_{11} is an icosahedron with one missing cap, Si_{12} is a complete icosahedron, Si_{13} is a surface capped icosahedron, Si_{14} is a 4-4-4 layer structure with two caps, Si_{15} is a 1-5-3-5-1 layer structure, and Si_{16} is a partially closed cage consisting of five-membered rings. The characteristic feature of these clusters is that they are all surface.

Smalley and co-workers discovered that chemisorption reactivities of silicon clusters vary over three orders of magnitude as a function of cluster size. In particular, they found that Si_{33}, Si_{39}, and Si_{45} clusters are least reactive towards various reagents compared to their immediate neighbors in size. We provide insights into this observed reactivity pattern through our stuffed fullerene model. This structural model consists of bulk-like core of five atoms surrounded by fullerene-like surface. Reconstruction of the ideal fullerene geometry gives rise to fourfold coordinated crown atoms and π-bonded dimer pairs. This model yields unique structures for Si_{33}, Si_{39}, and Si_{45} clusters without any dangling bonds and thus explains their lowest reactivity towards chemisorption of closed shell reagents. We also explain why a) these clusters are substantially unreactive compared to bulk surfaces and b) dissociative chemisorption occurs on bulk surfaces while molecular chemisorption occurs on cluster surfaces. Finally, experiments on Si_xX_y (X = B, Al, Ga, P, As, AlP, GaAs) are suggested as a means of verifying the proposed model.

1 Introduction

Nanometer size particles are the embryonic forms of matter whose microscopic study provides insights into the evolution of material properties from molecules and surfaces to solids [1, 2, 3, 4]. Furthermore, nanoscale particles have been shown to exhibit exotic optical properties and reactivities quite different from those in molecules and solids [1, 2, 3, 4, 5, 6]. For these reasons, theoretical studies on clusters are critical to the design and synthesis of advanced materials with desired optical, electronic, and chemical properties. Such studies are at the interface of the traditional fields of quantum chemistry, solid state chemistry, and statistical mechanics. Hence, physicists, chemists, and material scientists are working individually and in teams to unearth the fundamental principles underlying the structure, dynamics, and reactivities of these clusters [3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. Indeed, the diverse group of scientists assembled at this NANOMEETING-95 is testimonial to the

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breadth and depth of scientific inquiry into this novel state of matter.

The nanoscale semiconductor clusters have potential applications in non-linear optical devices, photovoltaic devices, and as photochemical catalysts. For this reason, intense experimental activity exists on the synthesis, structural characterization, spectroscopy, and reactivities of these clusters. On the other hand, the theoretical and computational efforts on these systems are at a primitive stage. In particular, due to both experimental and theoretical limitations, the detailed knowledge of the role of surface structure on the reactivities of these nanoparticles is lacking. To correct this imbalance, we started a systematic theoretical investigation of the structure-reactivity relationship in semiconductor clusters. The results from these investigations is the subject of this Article.

2 Structures of small silicon clusters

Since naked silicon clusters are highly reactive, they are mostly synthesized in a molecular beam under high vacuum conditions [5, 6]. The number density of available clusters is so low that diffraction based structural investigations are not feasible under these experimental conditions. Theoretical calculations have now established the structures of Si_N clusters in the $N = 2$-10 atom size range [14, 15]. These calculations have employed quantum chemistry molecular orbital techniques. While these methods are accurate for structural determination, computationally they are highly cpu intensive and hence it is difficult to search all possible cluster geometries. Consequently, we employed the tight-binding molecular dynamics (TB-MD) simulations for the determination of the

ground state structures of Si_N clusters in the $N = 11$-16 atom size range. The results of these simulations are presented below.

The choice of the tight-binding method for the study of the cluster structures is motivated by its accuracy and computational efficiency [16, 17, 18, 19]. This all valence electron method is equivalent to the extended Hückel method well known in theoretical chemistry [20]. This method has yielded structures in excellent agreement with *ab initio* electronic structure calculations for both carbon and silicon clusters [16, 17, 18, 19, 21]. Recently, Menon and Subbaswamy have constructed an accurate tight-binding Hamiltonian for silicon clusters [18, 19]. This Hamiltonian includes Harrison's universal parameters appropriate for the description of bulk Si [22], supplemented with two to four additional parameters for the description of the silicon clusters. These additional parameters are derived by fitting to the Si_2 bond length and vibrational frequency and to the overall size-dependent cohesive energy curve of clusters [18, 19]. Most importantly, none of the parameters of this Hamiltonian are fit to any of the cluster structures. Full details of the Hamiltonian and computational methods are described elsewhere [18, 19].

As the size of the cluster grows, the number of structural isomers increases exponentially, with the result that searching the complete configuration space for the global potential energy minimum becomes a formidable task. However, by combining the tight-binding method with the molecular dynamics [23] simulated annealing technique we can efficiently search the cluster configuraton space and determine the ground state geometry [24, 25]. We used this TB-MD method in all the calculations reported here.

Figure 1 displays the lowest energy structures obtained using this TB-MD technique for clusters in the $N = 11$-16 atom size range. The Si_{11} structure consists of two tetragons in

the anti-prism geometry and three caps. Two of these caps are attached to the opposite faces of the two tetragons, while the third one is attached to the edge of the top tetragon. This structure may also be described as an icosahedron with one missing atom. Replacing this missing atom would give rise to the icosahedral cage structure for Si_{12}. Such a spherical cage structure has not been predicted or observed for any of the 12-atom elemental clusters. Adding a face cap to Si_{12} gives the lowest energy Si_{13} structure. An alternative structure, derived by placing a Si atom inside the cage of Si_{12}, is a high energy local minimum.

Adding a face cap to the Si_{13} structure does not yield the lowest energy Si_{14} structure. Instead, Si_{14} assumes a layer structure consisting of three planes of four atoms each and two adjacent face caps. By suitably rotating this structure, we may also describe it as a pentagon sandwich (or prism) with two caps each at the top and the bottom. The pentagon prism is somewhat distorted and displaced. We also considered a bi-capped hexagonal anti-prism as a candidate for the ground state of Si_{14}. However, this structure proved to be unstable, indicating that six-atom ring structures are still not favored in these small clusters. Like Si_{14} cluster, Si_{15} assumes a layer structure consisting of 1-5-3-5-1 layers. However, Si_{16} is quite unlike any of the previous clusters. It is an open cage consisting of fused pentagons, reminiscent of the small fullerenes.

3 Stuffed Fullerene Model

Searching the complete configuration space for the ground state structures is very difficult for large clusters, even with the TB-MD method. Consequently, we propose a simple model that explains the trends in the reactivities of silicon clusters in the 30-50 atom size regime. We call this the stuffed fullerene model [26]. This model consists of 1) a central atom A, 2) four atoms B surrounding A in tetrahedral geometry, and 3) fullerene surface. The B atoms bind to twelve surface atoms, thus rendering the B atoms also bulk-like with four-fold coordination and tetrahedral geometry. The surface then relaxes from its ideal fullerene geometry, the same way the (1×1) bulk surfaces relax. This relaxation gives rise to crown atoms and dimers (CAD) pattern on the surface. The crown atoms are formally three-fold coordinated and possess one dangling bond each. The dimers are also formally three-fold coordinated, but they eliminate their dangling bonds through π bonding. The essential feature of this construction is that the bulk-like core of five atoms (A + B) and fullerene-like surface make these structures stable. In principle, this model is applicable to clusters containing more than twenty atoms.

Unlike carbon, silicon does not form strong delocalized π bonds [27]. Consequently, fullerene cage structures [28, 29, 30] are energetically unfavorable for silicon clusters [31]. Instead, intermediate sized silicon clusters prefer σ-bonded network structures similar to the diamond structure of bulk silicon [31]. The fullerene geometry for the surface, consisting of interlocking pentagons and hexagons, gives special stability to the surface atoms [29]. Furthermore, since delocalized π bonding is not favorable in silicon, we expect the surface atoms to relax from their ideal fullerene geometry to allow for dimer formation through strong local π bonding. Our model accounts for all these facts.

We generate the Si_{33} structure by stuffing the 5-atom core inside the Si_{28} fullerene cage. We orient the 5-atom pyramid in such a way that the central atom A, the core atom B, and the crown atom C lie on a line. The crown atom is at the center of three fused pentagons and it is surrounded by three other

surface atoms D. The D atoms now relax inwards to form the B-D bond. The same type of relaxation motion is necessary to form the 2×1 reconstruction on the bulk Si(111) surface [32, 33]. The activation barrier of ≈ 0.01 eV [32, 34] for this relaxation is easily recovered by the formation of the B-D bond, whose strength is 2.3 eV/bond [27, 33]. Consequently, such a relaxation of fullerene surface is feasible even at 100 K. Finally, the remaining surface atoms E readjust to form as many dimers as possible. Similar relaxation motion and dimer formation occurs on Si(100) surfaces also [33, 35]. The dimers are σ-bonded pair of atoms whose dangling bonds are saturated through the formation of π bonds.

The structures of Si_{33}, Si_{39}, and Si_{45} clusters thus generated are displayed in Fig. 2. These structures reveal that the crown atoms are able to form a fourth bond to the core atoms B, thus rendering the B atoms formally five-fold coordinated. The B-C bond arises from the back donation of the electrons from C to B and it weakens the neighboring bonds through electronic repulsion. We do not know the strength of this back bond, but it is sufficiently strong to eliminate the dangling bond on the crown atom and make these magic number clusters unreactive.

Chemisorption is sensitive to the local electronic structure and chemical bonding on the surface. On bulk Si(111)-(7×7) surface, chemisorption occurs preferentially on rest atom sites and less on crown atom sites [36]. Absence of rest atoms in silicon clusters is the main reason why these clusters are much less reactive than bulk silicon. Furthermore, dissociative chemisorption of ammonia on bulk Si(111)-(7×7) surface is due to the close proximity of the rest atom and crown atom sites [36]. Absence of such a configuration on silicon clusters explains why reagents are unable to dissociate on the cluster surfaces; instead they chemisorb molecularly. We predict

that the alloy clusters $Si_x X_y$ (X = B, Al, Ga, P, As, AlP, GaAs) will be highly inert and that it may be possible to synthesize these in macroscopic quantities. We suggest experiments on these alloy clusters as a means of fully exploring the role of surface structure on reactivities.

4 Summary

In summary, we determined the structures of small silicon clusters through TB-MD simulations. These simulations revealed that Si_{11} is an incomplete icosahedron, Si_{12} is a complete icosahedron, Si_{13} is a surface capped icosahedron, Si_{14} is a 4-4-4 layer structure, Si_{15} is a 1-5-3–5-1 layer structure, and Si_{16} is a partially closed cage consisting of fused pentagons, reminescent of small fullerenes. The atoms in all these clusters strongly prefer to lie on the surface rather than inside.

We also propose a novel structural model to explain the experimental data of Smalley and co-workers on the chemisorption reactivities of silicon clusters towards various reagents [5]. This model consists of bulk-like core of five atoms stuffed inside reconstructed fullerene cages. The resulting structures of Si_{33}, Si_{39}, and Si_{45} are unique, have maximum number of four-fold coordinated atoms, minimum number of surface atoms, and zero dangling bonds. This model does not yield such unique structures for other intermediate sized clusters and hence they will have larger number of dangling bonds. This explains why Si_{33}, Si_{39}, and Si_{45} clusters are least reactive towards reagents with closed shell electronic structure, such as ammonia, methanol, ethylene, and water [5]. We suggest that experiments on alloy clusters are needed to fully understand the role of surface structure on the chemical reactivities of these nanometer size particles.

Acknowledgments

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Figure 1: The lowest energy structures of Si_N ($N = 11\text{-}16$) clusters, determined using the tight-binding molecular dynamics simulated annealing technique.

Figure 2: Structures of the least reactive clusters, Si_{33}, Si_{39}, and Si_{45}, obtained using the proposed stuffed fullerene model. These clusters do not possess any dangling bonds and hence are least reactive towards reagents with closed shell electronic structure, such as ammonia, methanol, ethylene, and water. Representative atoms in different chemical environments are labeled from A to E.